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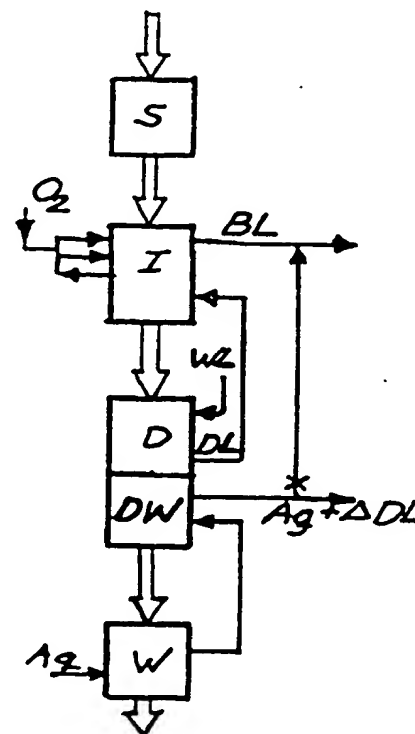
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(54) Title: SULPHIDIC IMPREGNATION OF CHIPS FOR ALKALINE PULPING

## (57) Abstract

Method of stepwise delignification of lignocellulose fiber material by digestion with sulphidic alkaline liquor comprising kraft cooking of wood chips with white liquor. White liquor is distributed during digestion. Ex-digestion liquor is displaced from digester pulp at low or no dilution by any brown stock pulp washing medium and piped to initial chip material impregnation stage. Hereby pulp yield and viscosity values are improved. These may be enhanced by polysulphide which stabilizes carbohydrates. Such polysulphide reaction is produced by in situ oxidation. Black liquor at reduction degree attained by impregnation is passed to the recovery plant while a portion of ex-digestion liquor at its original reduction is directly recycled together with impregnated material. Separately from extraction of ex-digestion liquor, liquor containing the washing medium is removed and passed to concentration and combustion steps which optionally are arranged after admixture to black liquor.



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Sulphidic impregnation of chips for alkaline pulping

- Manufacture of papermaking pulp from lignocellulose fiber materials by alkaline delignification in digesters is successively being modified in regard to processing of chemicals. Black liquor (BL) is recovered for regeneration of alkali and sulphur compounds from white liquor (WL) which is distributed to various delignification stages. The present invention refers to kraft pulp cooking of wood chips and also applies to versions using sulphidic alkaline cooking liquors enhanced by various additions, such as polysulphide (PS), sulphite, anthraquinone, methanol and others.
- Normal cooking yield of pulp, i.e. brown stock (BS), ranges from 40 to 60% on wood, all calculated on a moisture-free basis. Bleached soft wood pulp was produced at an average yield of 45% before environmental regulations required extended cooking which decreases bleached yield to about 42% or lower. Hardwood yields bleached pulp on a higher level at an average of 50% on wood. Inclusion of PS in cooking liquor can give a pulp increment of 10-15% (on ordinary pulp) from a given quantity of wood but would require means to prevent emission of acidic and/or odorous sulphur compounds from BL processing. Too advanced yield increase of bleached pulp produces some non-desirable paper qualities, such as lower opacity and tear strength approaching that of (acid) sulphite pulp.
- For some time, kraft pulp mills have reduced water pollution by modification of cooking to produce low kappa brown stock for bleaching. This is accomplished with a certain selectivity in regard to concurrent degradation of cellulose, measured as viscosity on a solution thereof, for which originally a limit of  $900 \text{ dm}^3/\text{kg}$  was set but which is successively being lowered. However, yield of pulp, counted on wood, suffers.

A novel method is described here, giving improved pulp yield at any given brown stock kappa number by more efficient utilization of the sulphidic compounds as regards WL, commonly as  $\text{Na}_2\text{S}$ , together with wood hemicel-  
5 lulose. The successive steps in present pulping technology and the novel improvement thereof is shown in Figure 1, wherein schemes I-V are as follows:

- S = Steaming of chips  
10 I = Impregnation of chips by process liquor  
D = Digestion (cooking) of impregnated chips  
DW = Digester washing comprising displacement in digester of ex-digestion liquor to be distinguished from previously known displacement of BL (black liquor) from  
15 BS (brown stock) to recovery plant  
W = Any additional washing of pulp after DW, so far often on open drum filters, to produce BS  
WL = White liquor (alkaline delignification liquor)  
BL = Black liquor at pertinent concentration passed to  
20 recovery plant for regeneration of WL alkali.  
Optional recycling of some portion of BL to digestion  
DL = Ex-digestion liquor circulating within D-system and which is successively converted to BL  
25 Aq = Aqueous washing medium, e.g. condensate from process liquor evaporation and preferably filtrate from subsequent pulp washing stages such as from oxygen delignification or bleaching  
BL+Aq = Regular BL at some dilution reclaimed from  
30 pulp and passed to recovery plant  
Aq+DL = Major portion of washing medium and dilute minor proportion of DL from pulp to recovery plant  
BL from I = BL of DL from chips to recovery and essentially Aq-free.

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For certain kraft process steps, the term reduction or reduction degree applies, which refers to sulphur equiva-

lents present as percentage of sulphide to total sulphur. According to the state of the art, reduction declines in the course of digestion to a major extent by disproportioning reactions and is at its lowest level in evaporated BL. The highest level is reached in (by reductive combustion of BL recovered) soda product prior to its dissolving in green liquor preparation. When liquor is exposed to air, reduction declines down to about 85% when soda smelt is dissolved in green liquor and then in recausticizing plants of past design, depending on how well various forms of catalytic metals and contact to air oxygen are avoided. The admixture of BL from brown stock washing to WL at charge of regular cooks decreases reduction under WL level. Although the BL/WL mixture occasionally may be tested on sulphidity, its reduction degree has previously not been found of interest but the WL reduction value could well be halved at said conditions. The standardized term sulphidity expresses  $\text{Na}_2\text{S}$  as percentage of active alkali =  $\text{AA} + \text{Na}_2\text{S}$ , all calculated as equivalent  $\text{NaOH}$  ( $\text{OH}^-$ ). This term is useful for fresh WL but somewhat misleading when applied to the progress of cooking when  $\text{OH}^-$  from both AA components is consumed. Another common kraft liquor process term is oxidation degree which is related to oxidation of BL sulphide to produce more stable thiosulphate and prevent losses of sulphur compounds in non-condensable gases and is calculated as percentage on sulphide in non-oxidized BL.

Brown stock (BS) refers to fully washed pulp, discharged from digester and sometimes called "unbleached pulp". Incompletely washed or non-washed pulp is, according to prevailing technique, obtained together with black liquor (BL). Some pioneering technologists rightly applied the term "black stock" for its treatment in effluent-free systems. By now, the term "hot stock" refers to suspension prior to the last washer in a series of washers delivering brown stock for bleaching. Novel features of

this invention necessitate that digested chips prior to defibering into a suspension are designated digester stock.

5     Scheme I of Figure 1 exhibits regular batch cooking with steaming (S) at digester chip filling, followed by charge of WL and BL filling to prescribed ratio liquor/wood. This ratio is in general 3/1 to 4/1, but may be lower, about 2/1, when vapour phase cooking is applied on parti-  
10     cularly impregnated chips. Temperature rising schedule comprises initial phase impregnation, followed by, often stepwise, increase to maximum temperature. Appropriate combination of cooking variables is performed by means of the H-factor according to Vroom, formulated on kinetical  
15     grounds.

Earlier versions of cooking featured transfer of BL at certain pressure to next digester charge, while other versions utilized alkali counter-currently. At the time,  
20     it was found that equilibrium concentration of delignification products formed by BL backfill at least did not impair pulp quality properties. When sulphidity was about or over 25%, no reason was found for practicing any modification, proposed at the time, involving multiple-  
25     digestion using white liquor injection. Reclaimed BL that is diluted by washing medium (Aq) is used for digester filling to pertinent liquor/wood ratio as well as for transport of black stock via a blow tank to a washing plant (W).

30     Scheme II shows reclaiming of BL directly from batch digester stock by in-digester displacement (DW) and flushing stock with temperate filtrate from brown stock washing (SE patent 139 301, Mannbro, N.V.). Progress is  
35     rapidly made for modified cooking systems based on in-digester displacement of BL of which a portion is recycled for impregnation of chips to be digested by injec-

tion of WL. This type of modified cooking facilitates extended delignification to low kappa number, although the yield of pulp in percentage calculated on wood, decreases. Among the means to prevent this loss in yield,  
5 an increase is proposed of not only sulphidity but also actual concentration of sulphide in the impregnation liquor, which may produce a gain in yield by 0.5-1%.

Scheme III refers to continuous cooking. For clarity,  
10 directions of liquor flows through the material in the digester are omitted from the scheme. Presumably at most mills WL is still charged, wholly or to a major part, to impregnation liquor circulation. However, presumably in regard to sulphide-concentration and consequences on  
15 sulphidity at modified WL alkali distribution, some recirculation of diluted BL from DW (indicated by hatched line) is considered elsewhere (SE patent application 8804578-6, Backlund, Å.). Another but straight counter-current system employs total recycling of BL for impreg-  
20 nation (SE patent application 9001783-1, Richter, J.C.F.C.). For closed cycle operation between cooking and alkaline oxygen delignification (oxynation) a similar method has been described (US patent 4,155,806, Mannbro, N.V.). Both are, however, impaired by passing washing  
25 medium (AQ) through digestion (D).

It is noted that for some cases of continuous cooking using WL in impregnation stages, the spent liquor is recycled as such through recausticizing plant. Digester  
30 heating is performed by vapour recompression. Another version employs green liquor in an initial stage of digestion and withdrawn liquor is causticized.

Scheme IV shows particular recycling of ex-digestion  
35 liquor (DL) to the impregnation stage. The hemicellulose recycling increases somewhat pulp yield (SE patent from application 2823/66, Croon, Dillén and Noréus). However,

all WL is also charged to the impregnation stage and all BL is reclaimed from DW diluted by Aq from brown stock washing. The patent discloses addition of separately prepared polysulphide solution for stabilizing hemicellulose in impregnation of softwood and birch chips. The latter gave a particularly increased yield of bleached pulp.

#### The present invention

10 Scheme V. Ex-digestion liquor (DL) is withdrawn and is split into two flows in connection with the chips impregnation stage. One flow is counter-current to chips from steaming (S) and reacts with chips, while the other displaces reacted impregnation liquor from chips and else  
15 recycles with or remains with chips for digestion (D) with WL. By impregnation reactions of wood components, the DL is converted to black liquor (BL) which is withdrawn directly from the wood chips, and passed to the  
20 recovery plant for generation of alkali. Non-withdrawn DL is as residual DL ( $\Delta$ DL) reclaimed from brown stock washing (W) of digester stock and is hereby diluted by an extensively larger volume of Aq. Hence Aq+ $\Delta$ DL bypasses digestion to alkali regeneration plant.

25 Continuous digesters of type Kamyr feature split charge of white liquor and application of zones for concurrent and counter-current flows, as regards movement of liquor relative to the fibrous material, as well as zones where  
30 flows meet for withdrawal of liquor. According to the present invention, counter-current flow through layer of chips by BL produced from DL is preferred. Similarly, counter-current flow of washing medium (Aq) through digester pulp is used for displacement (DW) of digestion  
35 liquor (DL).



According to the invention, a volume of sulphidic white liquor, determined by its concentration of hydroxide (effective alkali), is added to the impregnated chips and considered together with alkali in recycling DL in reaction with chips. The resulting sulphide equilibrium concentration is utilized by the recycled fraction reacted with feed of chips to the impregnation stage (I). (In Scheme V, O<sub>2</sub> indicates addition of oxygen or oxygen containing gas to sulphidic impregnation liquor reacting with chips. This relates to an alternative oxidative conversion of sulphide to partial formation of polysulphide as dealt with further on.)

In Schemes I-V washing medium (Aq) is often used, comprising effluent filtrate from alkaline oxygen delignification stage in an effluent-free brown stock treatment system between digestion and O-stage (US patent 3,830,688, Mannbro, N.V. - Validity confirmed by owner's request for re-examination). O-stage filtrate is commonly used for displacement of BL from brown stock and is then included in BL passed to alkali regeneration plant. Effluent-free operation is facilitated when carry-over with washed brown stock is derived from ex-digestion liquor (DL) rather than from black liquor (BL). Alkali required in the O-stage is mostly prepared by WL oxidation using oxygen containing gas to such an extent that reduction degree approaches zero. Regeneration of alkali free from almost any sulphur compounds is being developed and such alkali may also be used for final stage cooking and extraction stages of the bleaching sequence.

Abatement of odorous gases emitted from digestion and from BL suspensions prior to O-stage, differs according to condensing and alternative blow and flushing system and some cooling of digester discharge liquor may be arranged for WL pre-heating. However, according to Scheme

V any such condensing or pre-heating system is moved to impregnation system.

5 The term iso-thermal cooking previously denoted pre-heating of liquor for continuous cooking at a constant temperature, although it is now applied to extended delignification at relatively maintained temperature and alkalinity in a zone of continuous digester previously used for displacement washing. The DW zone of Scheme V  
10 improves the extended delignification because of the early removal from the impregnation stage of BL solids. Originally, the term extended cooking referred to methods for bringing down brown stock kappa prior to oxidative bleaching, in order to avoid or reduce formation of  
15 organic chlorine compounds in bleach plant effluent. When this has been accomplished, the new issue now reduces costs for oxygen based bleaching agents, such as peroxide. Scheme V is instrumental in fulfilling this aim, although separate combustion of bleachery filtrate included in the final filtrate (Aq+ADL) facilitates handling of chlorine compounds.  
20

The impregnation stage (I) shown in Scheme V is not limited to physical impregnation of liquor in the voids  
25 of the material but comprises chemical reactions significant to the initial phase of cooking. For the progress of a cook, three phases can usually be distinguished: 1) initial phase, 2) bulk delignification and 3) final delignification. Initial impregnation is optionally  
30 performed in a digester vessel or separate vessels are used as an alternative. Impregnation for batch cooking is preferably performed in each digester. Continuous cooking has developed into use of a separate zone or vessel for impregnation and sometimes an additional  
35 vessel for the initial phase.

In the impregnation/initial stages about 60% or more of the total charge of alkali (hydroxide) is consumed under a relatively short time and mainly by reactions dissolving carbohydrate (hemicellulose). Dissolution of lignin is hereby non-selective and the wood ratio lignin/carbohydrate remains until bulk delignification. The lignin reacts, however, initially with sulphide (hydrosulphide and hydrogen sulphide respectively) in such a way that its dissolution by hydroxide in the later stage is promoted (Olm, L. and Tistad, G.: Svensk Papperstidning 1959, nr 15, pages 458-464). It is noted that impregnation may be performed by addition of  $H_2S$  according to known methods. Oxidation of sulphidic compounds prevents their emission to atmosphere and polysulphide can be produced, as dealt with further on.

In any impregnation stage alkali reacts with acidic groups of pertinent wood material, i.a. under formation of acetate, and with saponifiable extractives. According to presently practiced technique, all these products pass through digestion stages to be removed with black liquor reclaimed from digested stock. Many brown stock washing investigations also prove slow removal of soap from brown stock. According to the present invention, the major part of said dissolved wood products is removed from chips prior to delignification which efficiently contributes to selectivity of final purification for bleaching and avoidance of pitch in stock systems.

Manifold observations show the importance of final delignification holding low concentration of dissolved wood components, essentially lignin, and of  $Na^+$  while concentration of  $OH^-$  should be sufficient for delignification. This applies to preventing lignin absorption on fiber as well as simultaneous cellulose degradation. Hereby bleached pulp cellulose viscosity is impaired, which indicates loss of potential paper strength pro-

perties. Recent environmental regulations lead to modifications of digestion to further lowered kappa but O-stage delignification is, in this respect, very sensitive to carry-over of dissolved wood products with brown stock, which, however, according to the invention, to a major part never entrain the carry-over contributing digestion liquor.

Digestion heat economy is favoured by the direct charge of ex-digestion liquor (DL) to impregnated chips which join with hot white liquor (WL). Less steam is required for heating because resulting cooking liquor is not subjected to dilution by washing medium (Aq) which, as far as volume balance of digester system allows, is passed directly to plant for concentration, evaporation and alkali regeneration.

The cooking mixture of chips and new cooking liquor will have a temperature that, besides any pre-warming and steaming of chips, depends on the withdrawal of heat with BL from the impregnation stage which derives from digestion. BL heat can be directly utilized for multiple effect evaporation or optionally flashed for steaming of chips. When thin liquor of washing medium (Aq+ $\Delta$ DL) is sufficiently free from chloride forming substance, it may be mixed with black liquor for common evaporation.

Some versions of batch cooking, e.g. so called low energy cooking, are designed for pre-warming of chips by some used displacement liquor. Alternatively, this liquor could be subjected to separate pre-evaporation, i.a. to thermo-compression evaporation within the limits for acceptable boiling point rise. Mechanical compression can possibly be gas turbine powered.

It is feasible to use thin liquor as solvent for recovered soda smelt and causticize the solution to form "whi-

te" liquor (WL). Optional evaporation of WL for separation of dead-load Na-salts would be within the frame of heat economy. Anyhow, when facing huge investment in a soda recovery boiler, an alternative would be an additional, preferably oxidative, combustion of evaporated Aq+ADL. Hereby produced combustion residue of soda, sulphate etc. could be passed to the kraft recovery process. When the soda content of the residue so qualifies, it may be causticized to liquor free from sulphide and other reducing matter and thus useful for bleaching. Gassification of black liquor for combi-power generation based on energy-rich BL and mechanical thermo-compression can be attractive in the future.

15    Impregnation together with conversion of sulphide to polysulphide

Impregnation in the presence of polysulphide (PS) is practiced according to various methods. Thus, it is disclosed that sulphide supplied as  $\text{Na}_2\text{S}$  in white liquor (WL) contributed to delignification of increment PS pulp at given kappa number and denoted as a threshold effect. Elsewhere anthraquinone was introduced as a delignification accelerating agent while PS stabilizes hemicellulose and their combination is considered to give synergistic effect and the addition should be made for long residence in the digestion system by avoiding dilution, which otherwise is caused by a washing medium.

30    Hemicellulose stabilization is, as is well-known, attained by reacting polysulphide (PS) according to Scheme IV. Separately prepared PS, either from elemental sulphur or PS essentially deriving from sulphide, is used. Elimination of particular sulphur compounds to generate PS is developed according to other methods. Hence, oxidation of sulphidic liquor or mixture of liquors by oxygen containing gas and in the presence of chips proved simple and

satisfactorily efficient. The kraft process produces fundamentally white liquor (WL) at a high reduction degree to form cooking liquor of high delignification efficiency which, however, is more or less lost by any  
5 prior PS oxidation of WL sulphide as such or as a cooking liquor component.

The present invention features application of ex-digestion liquor (DL) for impregnation of chips which, in  
10 turn, can be combined with oxidative PS reaction with no harm attaching to the reduction degree and sulphidic values contributed by fresh white liquor (WL). Alkali remaining in ex-digestion liquor (DL) is utilized for BL forming reactions with wood and at a pertinent temperature after partial ex-liquor recycling determined by the  
15 ratio volume of cooking liquor/wood required at the digestion stage.

Black liquor viscosity during evaporation is primarily  
20 related to its alkalinity, and some addition of alkali, during or after impregnation, could be justified. Alternatively, the viscosity may be lowered by pressure heating of the black liquor, whereby, in some cases, sulphidic gaseous compounds are expelled. These techniques are  
25 currently being practiced for evaporation of up to 80-85% solids on total liquor.

It is commonly acknowledged that lignin in pulping liquors via quinone reactions oxidizes sulphide, i.e.  
30 hydrosulphide ions, to polysulphide (ions) which stabilize hemicellulose in the lignocellulose material as well as some hemicellulose dissolved at certain phases of digestion. When polysulphide is formed in the presence of wood components, optimization is reached by readings of  
35 the equilibrium expressed as redox-potential and pH for the purpose of which sonds are found on the market. They are designed for on-line application and redox sonds are

practiced for regular thiosulphate oxidation of BL. Such full oxidation may be performed on BL discharged from impregnation or alternatively, as an additional stage to PS oxidation in the presence of chips.

5

In-line oxygen injection to the total volume of ex-digestion liquor in a closed system prior to impregnation is disclosed by SE patent application 9102834-1 (Mannbro, N.V.). Such a closed system PS-oxidation requires concentrated oxygen, preferably over 90% in volume. Recently developed ozone bleaching uses oxygen as carrier gas which may then be utilized in the pulping process and eventually for PS generation according to the invention.

10

15 Sulphidic impregnation according to the invention may, in its PS version, use air in agitators such as at screw feeding of chips through certain horizontal or inclined digester tubes of known design. These are also suitable for flow of air or oxygen containing vapour through the connecting chip steaming stage. Low concentration of oxidizing agent but still almost closed system is accomplished by injection of concentrated oxygen and optional degassing to some combustion stage. For safety reasons, it is important that turpentine and volatile combustibles from wood and vapour condensate are treated separately from oxygen. Sulphur compounds present in odorous process gases are, according to certain publications (Teder and Tormund, Svensk Papperstidning 1983, R 198), reacted by polysulphide. The possible use of vapour from oxidized BL for steaming of chips without odour emission is noted.

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Some previously disclosed systems for multiple operation of batch digesters feature successive displacement of cooking liquor and displacement liquors via accumulators and allow for polysulphide pre-treatment of chips (US patent 4,595,455, Mannbro, N.V.). Continuous digesters

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require modified extraction screens for transfer of ex-digestion liquor (DL) to the impregnation stage and separate discharge of surplus washing medium to plant for chemical recovery. The figure shown in SE patent application 9102824-1 exhibits a suitable continuous digester system except that recycling ex-digestion liquor admitted to digestion is oxidized. This will, of course, impair the reduction degree of cooking liquor mixture.

10    Example

Bleached softwood kraft pulp was produced by typical Kamyr-type impregnation and MCC (Modified Continuous Cooking) to brown stock kappa number 25 and oxygen delignification to kappa number 18, followed by bleaching according to the sequence (C+D)(EO)D for brightness 90% ISO. To reduce pollution from the mill effluent trials were performed to evaluate lowering the kappa number of stock from oxygen delignification stage to 14. This, according to parallel laboratory measurements, decreased the yield of bleached pulp from 43 to 42% on wood and viscosity from 900 to 830 dm<sup>3</sup>/kg. To establish means for improvement of said values, investigations within the frame of the present invention were performed by laboratory cooking and bleaching, simulating mill conditions after installation of impregnation stage using ex-digestion liquor as follows:

- 30    a) using at the mill established WL sulphidity = 35%.  
b) according to presumptions increased WL sulphidity = 45% resulting from improved sulphur balance by oxygen injection to impregnation stage with redox control.

Each series comprised a succession of 5 recycling batch cooks simulating equilibrium at MCC continuous cooking. The following results were obtained:



- a) at brown stock kappa 20 and kappa 12 after oxygen delignification, bleached pulp was obtained at a yield of 42% on wood and viscosity 890 dm<sup>3</sup>/kg,
- 5 b) at brown stock kappa 18 and kappa 12 after oxygen delignification, the yield of bleached pulp was 44% and the viscosity was 980 dm<sup>3</sup>/kg.

10 The charge of effective alkali in WL calculated in percentage on wood, moisture-free basis, was according to b) reduced by 5% as compared to operations established at the mill. Atmospheric emission of carbon dioxide is reduced in proportion to less dissolved wood substance and demand of regenerated alkali.

15 Results from the series of test cooks apply, on the choice of principle for bleaching for sequence, either ECF or TCF, whereby the latter encompasses stages for additional oxygen based bleaching agent such as ozone and peroxide. As to the TEF process, either an existent

20 alkali recovery capacity for combustion of TCF substance or a separate treatment of diluted residue of ex-digestion liquor containing Aq from washing medium deriving from bleachery filtrate is required. When treatment of the latter features separate evaporation, concentrated

25 filtrate may be combusted oxidatively as earlier disclosed by the present inventor (Mannbro, N., Nordic Pulp and Paper Journal Research Journal, 1989, pages 192-196 ibid. 1990, pages 134-141). Such TEF process again allows a total environmental concept for brown stock kappa

30 number about 35 and bleaching with efficient chemicals. These chemicals, particularly elemental oxygen and chlorine, are being manufactured at low energy demand and the pulp is produced at a bleached pulp yield of up to 45% or, according to the PS version, with 48% or higher

35 within the limits for potential paper strength.

CLAIMS

- 5 1. Impregnation of chips for sulphidic alkaline cooking of paper pulp whereby fibrous lignocellulose material, such as wood chips, is digested, preferably according to the known version utilizing one or more liquors prepared from by combustion regenerated delignification chemicals and of which at least two spent digestion liquor flows
- 10 are reclaimed separately for regeneration of delignification chemicals contained in liquors, of which one comprises sulphidic alkaline white liquor (WL), preferably at a reduction degree reached in the kraft recovery process and performed by stages a-f as follows:
- 15 a) at the impregnation stage (I) for, in connection with this stage, performed steaming of chips (S), the impregnation medium comprises a liquor compatible with the initial stage of digestion which is performed in one or more
- 20 stages in the digester to accomplish predicted delignification at partial dissolution of hemicellulose and formation of fiber pulp consisting of cellulose, hemicellulose and residual lignin;
- 25 b) the impregnation medium comprises ex-digestion liquor (DL) withdrawn at the lowest possible dilution and ideally displaced at no entrainment by washing medium (Aq) as conditioned by balance of digestion liquor volume and sulphide concentration;
- 30 c) black liquor (BL) is produced by conversion of ex-digestion liquor (DL) at the impregnation (I), and optional addition of a minor part of alkali required for digestion, said produced BL is withdrawn from feed of
- 35 chips to the impregnation stage and passed to the recovery plant for regeneration of alkali;

d) impregnated chips are reacted with alkali (WL) by admixture with respective injection to circulating digestion liquor, the flow of which is controlled according to the rate of progressing delignification of digester pulp;

5

e) the major part of ex-digestion liquor (DL) at prevailing concentration of sulphidic alkali is displaced or withdrawn respectively from digester pulp;

10

f) after displacement of ex-digestion liquor from digester stock, any liquor portion ( $\Delta$ DL) remaining in said stock, and a major part of soluble reaction products are reclaimed, e.g. by displacement washing and diffusion in consecutive steps, by application of washing medium (Aq),

15

deriving from the process vapour condensate in the form of a filtrate containing successively added solute substance, whereby the initial supply of medium (Aq) is performed counter-currently to the flow of brown stock, whereby it comprises the steps of

20

- governing the initial digestion liquor sulphidity by reduction degrees of charged liquors and sustaining the mixture of recycling ex-digestion (DL) liquor and white liquor (WL) prior to chip reaction practically close to that in the fresh white liquor (WL) having a reduction degree of about 90%;

25

- reacting wood acids and saponifiable extractives with alkali (OH<sup>-</sup>), the products being dissolved and/or dispersed in black liquor (BL) and in respect to Na<sup>+</sup> withdrawn with BL prior to digestion to avoid retarded selectivity; and

30

- reducing in respect to the earlier withdrawn BL components comprising formed solids and water from chip moisture, the volume balance of displacement and washing medium (Aq +  $\Delta$ DL and AQ) respectively, including a cycle of evaporating condensate.

35

- 5 2. A method according to Claim 1, wherein an inter-relating H-factor to supply of alkali and heat for digestion is favoured by partial ex-digestion liquor recycling at over-atmospheric pressure in connection with the feed of impregnated chips (from I to D).
- 10 3. A method according to Claim 1 or 2, wherein vapour released from ex-digestion liquor is used for steaming of chips (S), whereby vapour is released from the impregnation (I) or is flashed from an expansion vessel connected to the line for withdrawal of ex-digestion liquor (DL) from the digester.
- 15 4. A method according to any one of Claims 1-3, wherein impregnation (I, Scheme V) is performed in two or more steps, the first of which being performed at lower temperature than the following step, in which the temperature is approaching that of ex-digestion liquor.
- 20 5. A method according to any one of Claims 1-4, wherein the impregnation (I) is performed in the presence of polysulphide (PS), preferably in the first phase, for stabilizing carbohydrates in chips and hemicellulose in ex-digestion liquor (DL), and reaction products other than PS, i.a. thiosulphate and any sulphate, being with-
- 25 drawn with black liquor (BL).
- 30 6. A method according to Claim 5, wherein oxygen or oxygen containing gas for partial oxidation of sulphide to polysulphide (PS) is supplied and black liquor (BL) from the reaction with chips is passed to the recovery plant.
- 35 7. A method according to Claim 6, wherein oxygen (O<sub>2</sub>) is injected into the liquor by means of an in-line mixer, preferably into the flow of impregnation liquor passing through the chips in the impregnation stage (I), the

oxygen concentration being about or over 90% to control the loss of heat by pressure conditioned gas relief of i.a. inert gas.

- 5 8. A method according to Claim 6, wherein the mixture of chips and impregnation liquor being gaseous oxidized, preferably under agitation of the mixture by means of conveyers or screws for transport in horizontal or inclined digester tubes, whereby the oxygen concentration
- 10 is kept at a lower level than in air and relief gas is being passed through the chip bin or alternatively, the relief is practically eliminated by injection of concentrated oxygen to a volume of circulating gaseous mixture maintained in the system.
- 15 9. A batch digestion plant, comprising multiple digesters connected by a pipeline system, for liquors applied in a number of stages for impregnation and digestion from liquor accumulators permitting changes of liquor volumes
- 20 without any heat loss by expansion between digester vessels in phases from filling to emptying, whereby at least one of said accumulators is being arranged for passing ex-digestion liquor (DL) to chips for impregnation in the digester and ultimately as black liquor (BL)
- 25 being withdrawn to a plant for recovery of its content of heat, combustibles and chemicals, said plant optionally comprising vessel for flash of vapour required for chip steaming and/or a heat exchanger for heating of white liquor (WL) which is passed to the digester liquor system.
- 30
- 35 10. A continuous digestion plant, comprising a vertical cylindric main digester vessel through which chips and digester pulp pass through zones arranged for flows of digestion liquor, one zone at the discharge end of said vessel being arranged for flow of brown stock washing

filtrate as displacement medium counter-currently to digester pulp and said plant comprising

- 5     - a chip impregnation vessel (I) with separate outlets for recovery of black liquor (BL) and impregnated chips and an inlet for ex-digestion liquor (DL) a portion of which is being deviated to the impregnated chips and subsequent digestion;
- 10    - a main digester vessel with two or more inlets for white liquor (WL) to impregnated chips and digester pulp material respectively and an outlet from the zone for displacement of ex-digestion liquor (DL) which is passed to impregnation and to impregnated chips;
- 15     - a main digester pulp discharge zone with an inlet for washing medium deriving from brown stock washing and an outlet for ex-digestion washing thin liquor (Aq + DL);
- 20     - a volume control for the recycling of ex-digestion liquor together with chips charged with white liquor (WL) and the volume of washing medium (Aq) entrained at the displacement of said ex-digestion liquor.

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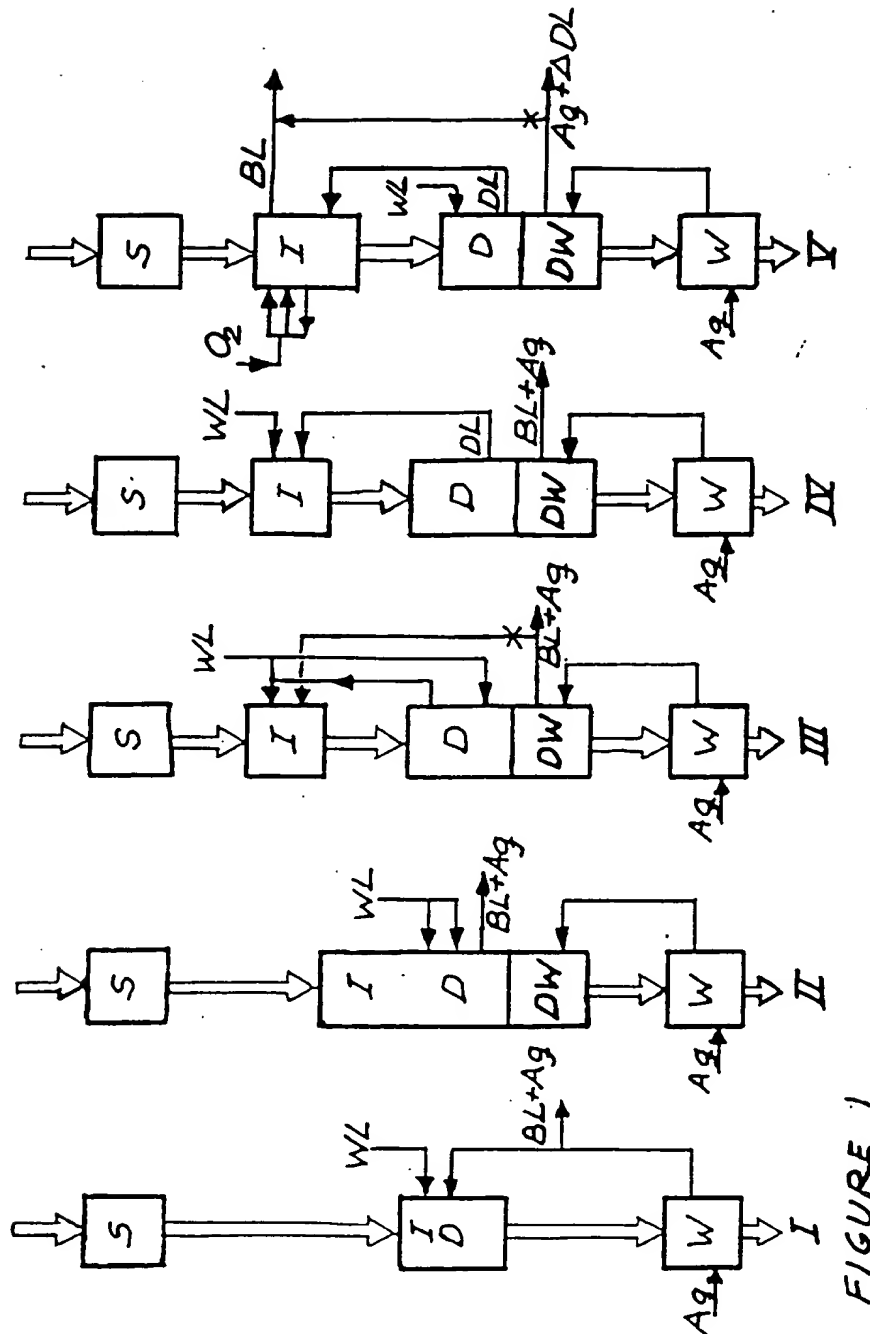


FIGURE 1

# SUBSTITUTE SHEET

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 95/00573

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 3/02, D21C 3/24, D21C 1/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SE 9102824 A (MANNBRO, NILS), 31 March 1993 (31.03.93), page 7, figure 1 ---	1-8,10
X	US 4595455 A (NILS V. MANNBRO), 17 June 1986 (17.06.86), column 6, line 58 - column 7, line 7, figure 1 --	9
X	US 5053108 A (JOHAN C.F.C. RICHTER), 1 October 1991 (01.10.91), column 1, line 44 - line 64, figure 3 --	1,3
X	EP 0527294 A1 (KAMYR, INC.), 17 February 1993 (17.02.93), column 3, line 33 - column 4, line 57 --	1



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

12 Sept 1995

Date of mailing of the international search report

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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

28/08/95

International application No.

PCT/SE 95/00573

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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EP-A1- 0527294	17/02/93	SE-T3- 0527294 AT-T- 115659 AU-A- 1492392 DE-D- 69200909 ES-T- 2067267 JP-A- 5195462 US-A- 5213662 US-A- 5346591	15/12/94 18/02/93 00/00/00 16/03/95 03/08/93 25/05/93 13/09/94